High frequency sound waves in vitreous silica

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We report a molecular dynamics simulation study of the sound waves in vitreous silica in the mesoscopic exchanged momentum range. The calculated dynamical structure factors are in quantitative agreement with recent experimental inelastic neutron and x-ray scattering data. The analysis of the longitudinal and transverse current spectra allows to discriminate between opposite interpretations of the existing experimental data in favour of the propagating nature of the high frequency sound waves.

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In the last 20 years great effort has been devoted to understanding the microscopic dynamics in topologically disordered systems. The need originates from the experimental observation that a large variety of glasses exhibits common dynamical and thermodynamical properties, which are anomalous with respect to the corresponding crystals [1]. In particular, around 5 K the thermal conductivity has a plateau and in the $10 \div 30$ K temperature range the reduced specific heat $C_P(T)/T^3$ goes through a maximum, indicating the existence of excess vibrations in the low-frequency range with respect to the Debye model. In a more extended range, below ≈ 10 meV, inelastic incoherent neutron [2] and Raman [3] scattering reveal a strong broad band, usually called *boson peak*, which can again be related to an excess of the vibrational density of states. At the present, a unique microscopic description of these excess modes does not exist and their theoretical interpretations include localized vibrational states [4], soft anharmonic vibrations [5], relaxational motions [2], intrinsically diffusive [6] and propagating [7] modes.

Among disordered systems, vitreous silica is a typical strong glass former and has widely been studied, both experimentally [2,3,7,8] and numerically [9]. The temperature analysis of the inelastic neutron-scattering intensity [2] suggested the coexistence of sound waves, below ≈ 4 meV, with a second class of local harmonic excitations, which become increasingly anharmonic towards the lowest frequencies. However, kinematic reasons did not (and do not yet) allow the use of the neutron scattering technique to directly study the acoustic excitations in the boson peak energy region. Only recently it became possible to utilize the inelastic x-ray scattering (IXS) with meV energy resolution [11] to measure the dynamic structure factor, $S(Q, E)$, in the first pseudo-Brillouin zone. Using this technique, the high frequency dynamics of v-SiO$_2$ at $T = 1050$ K has been studied in the $1 \div 6$ nm^{-1} momentum transfer range. The measured $S(Q, E)$ clearly indicate the existence of collective propagating excitations up to $Q = 4$ nm^{-1}, i.e. up to an energy of ≈ 13 meV. The energy of these excitations extends both below and above the boson peak region, located at $E \approx 4$ meV [7]. Recently this result has been confirmed in the whole $1800 \div 300$ K temperatures range [12]. At variance with this interpretation, analogous room temperature IXS data combined with non-kinematic inelastic neutron (INS) spectra [13] were interpreted as an indication of the existence of a cross-over from sound waves to localized acoustic modes, which should be responsible for the boson peak.

In order to clarify the propagating nature of low frequency modes around the boson peak region, this letter presents a molecular dynamics (MD) and normal mode analysis (NMA) study of the high frequency dynamics in vitreous SiO$_2$ in the $Q = 1.4 \div 5.1$ nm^{-1} range. The reliability of our investigation is validated by the good agreement of the calculated $S(Q, E)$ with the available INS [8] and IXS [7] data. The detailed knowledge of the spectral shape allows us to discriminate between the two proposed interpretations [7,13] and to establish the propagating nature of both longitudinal and transverse modes giving rise to the boson peak. Moreover, the widths of the excitations calculated in the harmonic approximation (i.e. via NMA) are in quantitative agreement with both MD and experimental data, indicating that in the examined Q range their origin is structural rather than dynamical.

Standard microcanonical MD simulations with periodic boundary conditions were carried out for systems consisting of 648 and 5184 particles enclosed in cubic boxes of length $L = 2.139$ nm and $L = 4.278$ nm respectively (mass density $\rho = 2.20$ g/cm^3). We used the two- and three-body interaction potential proposed by Vashista *et al.* [14] which, compared with the simpler-to-deal two-body potentials, gives a better description of the structural properties of SiO$_2$. Details of this study will be discussed in a subsequent paper. The electrostatic long range interactions were taken into account by the tapered reaction field method and the equations of motion were integrated with leap-frog algorithm using a time step of $\Delta t = 0.5$ fs. A β-cristobalite crystal was melted at $15,000$ K and equilibrated for a long time

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so that the initial state has no effect on the final configuration. The system was then cooled and thermalized through different temperatures ranging from 5000 K down to 300 K. The temperature dependence of the total internal energy and of the self-diffusion constants D_{Si}, D_O are studied to recognise the structural arrest, which is found at about 2700 K, a value definitely higher than the experimental glass-transition temperature [15] ($T_g \approx 1450$ K). This can be an effect, at least partially, of the quench rate [16], which in our MD simulation is much higher ($\approx 10^{13}$ K/s) than the experimental value ($\approx 10^2$ K/s). Two different techniques were adopted to study the dynamic of the system in the glassy state: i) (MD) the finite temperature ($T = 1500$, 1000, 600, and 300 K) atomic dynamics has been followed for 60 ps by recording the instantaneous configurations every 0.01 ps; ii) (NMA) the dynamical matrix has been calculated in a "glassy" (metastable) energy minimum, reached by the steepest-descent method [17], and then either diagonalized to obtain a complete set of eigenvalues and eigenvectors or used in the application of the spectral moments method [18,19].

We investigated the dynamical correlation in v-SiO$_2$ in terms of neutron- ($S_N(\mathbf{Q},E)$) and x-ray- ($S_X(\mathbf{Q},E)$) weighted dynamic structure factors. The presence of two distinct atomic species requires the calculation of the partial dynamic structure factors

$$S_{\alpha\beta}(\mathbf{Q},E) = \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{-i\omega t} \sum_{i\in\alpha}^{N_\alpha} \sum_{j\in\beta}^{N_\beta} \langle \frac{e^{i\mathbf{Q}\cdot\mathbf{r}_j(t)}}{\sqrt{N_\alpha}} \frac{e^{-i\mathbf{Q}\cdot\mathbf{r}_i(0)}}{\sqrt{N_\beta}} \rangle$$

where summation over i and j run over all atoms of type α and β respectively and $\mathbf{r}_j(t)$ is the position vector of atom j at time t. $S_{\alpha\beta}(\mathbf{Q},E)$ is easily evaluated from the MD trajectories. In the NMA one introduces the displacements $\{\mathbf{u}_i\}$ from the equilibrium positions $\{\mathbf{X}_i\}$ and expands these in terms of the normal modes; in the $\mathbf{Q} \cdot \mathbf{u}_i \to 0$ limit the *one excitation* contribution can be calculated as

$$S_{\alpha\beta}(\mathbf{Q},E) = k_B T \sum_\lambda \frac{\delta(\omega - \omega_\lambda)}{\omega^2} \times \quad (1)$$

$$\sum_{i\in\alpha}^{N_\alpha} \sum_{j\in\beta}^{N_\beta} \frac{e^{-W_{ij}}}{\sqrt{N_\alpha N_\beta m_\alpha m_\beta}} \mathbf{Q} \cdot \mathbf{e}_i(\lambda) \mathbf{Q} \cdot \mathbf{e}_j(\lambda) e^{i\mathbf{Q}\cdot(\mathbf{X}_i - \mathbf{X}_j)}$$

where the Bose-Einstein factor has been approximated by its classical limit, W_{ij} is the Debye-Waller factor and $\{\omega_\lambda\}$ and $\{\mathbf{e}_i(\lambda)\}$ are the eigenvalues and eigenvectors of the dynamical matrix of the system. $S_N(Q,E)$ and $S_X(Q,E)$ are then obtained by adding the partial dynamic structure factors weighted by the atomic species concentrations and by the corresponding neutron or x-ray scattering lengths. An average over the independent directions of $\mathbf{Q}$, i.e. $\mathbf{Q} = (\pm l, \pm m, \pm n)2\pi/L$, with l,m,n integer numbers, is also performed. The reliability of the harmonic approximation is probed by the good agreement existing between the $S(\mathbf{Q},E)$ calculated via NMA and via MD at finite temperature. Moreover, the systems with 648 and 5184 atoms give identical $S(\mathbf{Q},E)$ in their common Q range, indicating negligible size effects.

Fig. 1 compares in a very satisfactory way INS data (squares) of ref. [8] measured at 5.4 meV (corresponding to the position of the boson peak at $T \approx 1100$ K) with the neutron-weighted dynamic structure factor $S_N(Q,E)$ calculated by our MD approach at the same temperature.

We have also calculated the longitudinal current spectra $C_L(Q,E)$, defined as $C_L(Q,E) = E^2 S(Q,E)/Q^2$, at selected small Q values ($Q_{MIN} = 1.47$ nm^{-1} for the system with $L = 42.78$ Å). These spectra, reported in Fig. 2 for some low-Q values, have been fitted by the same model function (Damped Harmonic Oscillator, DHO) already used [7] to analyse the experimental spectral shape. In Fig. 3 we report as full circles the best fit values of the excitation energies $\Omega(Q)$, corresponding to the positions of the current spectra maxima, and of the excitation widths $\Gamma(Q)$. The form of the current spectra and the positions of the current spectra maxima are in qualitative agreement with those of [20]. The linear dispersion observed for $\Omega(Q)$ gives a longitudinal sound velocity which is slightly higher than that compatible with IXS data [7]; this could be due to the thermal history and quench rate of the numerical model, which can produce a tempering of the vitreous structure. The evident linear Q dependence of the current spectra maxima positions, as already observable from the raw data of Fig. 2, indicates the propagating nature of the excitations up to ≈ 20 meV, a range which includes the boson peak.

This finding is not in contrast with earlier INS results by Buchenau et al. [21], which demonstrate that pure plane-wave eigenvectors cannot explain the Q-dependence of the $S(Q,E)$ at $E \approx 4$ meV. Indeed, as it was shown also in other simulated glasses [22], the eigenvectors of propagating modes present a random uncorrelated component superimposed to the plane-wave.

There is quantitative agreement between the $\Gamma(Q)$ values obtained from our simulation and that measured by IXS for temperature ranging from 300 to 1800 K [12], both having a $\Gamma(Q) \propto Q^2$ behavior. The agreement of the $\Gamma(Q)$ values found in our *harmonic approximation* with those measured in the *real* and simulated system, strongly indicates that the excitations linewidth, in the investigated Q range, is likely to be related to the structural disorder rather than to anharmonicity or other dynamical effects. As suggested in ref. [7], the structural origin of the high frequency excitations widths is also supported by the temperature independence of $\Gamma(Q)$ derived from IXS data. The picture becomes more complicated at small Q. Although the $\Gamma(Q) \sim Q^2$ law found at temperature above ≈ 300 K by IXS and MD/NMA in the nm^{-1} range, quantitatively extrapolates over two decades in exchanged momentum down to the Brillouin

light scattering (BLS)range ($Q \approx 0.02$ nm^{-1}), suggesting a common structural origin of the $S(Q, \omega)$ linewidth, at $T < 100$ K the $\Gamma(Q)$ measured by BLS shows a strong temperature dependence [23]. Consequently, a structural origin of $\Gamma(Q)$ at high Q values is consistent with available data, while at small Q the dynamical effects could be predominant. At present we have no explanation neither for such different behaviour in different Q ranges nor for the $\Gamma(Q) \sim Q^2$ law observed at $T > 300$ K in the $Q = 0.02 \div 5$ nm^{-1} range.

In ref. [13], the localized nature of the high frequency excitations was derived from the lineshape analysis of the IXS data. However, the presence of a strong elastic contribution and the poor statistics, did not allow to discriminate between different lineshape models. A detailed lineshape analysis can be performed on the simulated $C_L(Q, E)$ spectra. In the inset of Fig. 4 we report an example of fits of our calculated longitudinal current spectra with the expression proposed in ref. [13]. Reliable fits can be obtained only leaving the important ω_{IR} parameter free. As reported in Fig. 4, the crossover frequency ω_{IR}, that according to the localization model should indicate the localization edge and therefore the boson peak energy, is strongly Q-dependent and assumes values definitely higher than that of the boson peak. If we impose the same value of the ω_{IR} parameter for the different Q spectra, the fits result unacceptably bad.

To investigate the nature of the propagating excitations giving rise to the boson peak, we have also calculated the transverse current spectra $C_T(Q, E)$ at selected Q values. The transverse spectra are not experimentally accessible and are obtained from the MD via the correlation function of the transverse current or from NMA substituting ($\mathbf{Q}\cdot$) in Eq. 1 with ($\mathbf{Q}\times$). The transverse current spectra are also reported in Fig. 2, where we observe the existence of a low energy excitation ($E \approx 4$ meV at $Q = 1.47$ nm^{-1}) which disperses with a sound velocity of ≈ 4300 m/s up to ≈ 15 mev at $Q=5$ nm^{-1}. The transverse modes become almost non-dispersing at $E \approx 20$ meV, an energy that is definitely higher than that characteristic of the boson peak. Also the propagating transverse dynamics may therefore contributes to the boson peak. It is worth to note that, in the Q range where the longitudinal and transverse modes show a propagating character, the spectra $C_T(Q, E)$ and $C_L(Q, E)$ show a marked difference, again indicating the non-localized nature of the vibrational modes. Indeed, for localized modes one should not expect any difference between "longitudinal" and "transverse" dynamics, being $\mathbf{Q}$ meaningless.

In conclusion, the numerical study of harmonic model of v-SiO$_2$ indicates that: *i)* The experimentally observed width of the excitations in the $Q = 1.4 \div 3.5$ nm^{-1} range is due to structural effects, i.e. to the fact that in this range Q is no longer a good quantum number in the topologically disordered silica. Anharmonicity or other dynamical effects (interaction with two level systems, soft potential modes, etc.) can only play a minor role. *ii)* Both longitudinal and transverse modes are propagating in the energy range covered by the boson peak: their dispersion relations saturate at much higher energy. *iii)* The explanation of the numerical data with a cross-over model gives a Q dependent cross-over energy which is inconsistent with the model itself. *iv)* The transverse and longitudinal dynamics keep their differences up to at least $Q = 5$ nm^{-1}, which indicates the non-localized nature of the vibrational states up to this Q-value.

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FIGURE CAPTIONS

Fig.1 - Q dependence of the inelastic neutron scattering from vitreous silica at 1.3 THz. The circle represent the data of ref. [8] at $T = 1104$K, the full line the results of the present NMA analysis multiplied by an arbitrary factor.

Fig.2 - X-ray longitudinal (line plus open circles) and transverse (line plus solid circles) current spectra obtained by the NMA at different Q values. Open and solid up-triangles refer to longitudinal and transverse spectra respectively, obtained by MD (216 SiO_2 units at 300 K). Full lines are the DHO fits of NMA longitudinal current spectra.

Fig.3 - a) Excitations energy $\Omega(Q)$ from the DHO model for the IXS data at $T = 1050$K (open circles) [7] and for the present NMA on the 0K configuration. b) As in (a) but for the full width at half maximum of the excitations $\Gamma(Q)$.

Fig.4 - Q-dependence of the cross over frequency ω_{IR} resulting from the fits of the localised modes model of ref. [13] to the longitudinal current spectra, calculated from NMA. The inset shows an example of the fit quality.